REMARKS

Status of Claims

In the Office Action issued July 18, 2003, a restriction requirement was issued, requiring election between Claims 1-23 and 36 (Group 1) and Claims 24-35 (Group II). Claims 1 - 23 and 36 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Hiroaki Otsuka et al. (JP63-183154) in view of Ullakko et al. (WO 97/03215).

In this Response, previous independent Claims 1 and 11 are amended and Claim 36 is amended from a previously dependent form into an independent Claim. Claims 2 – 4, 6, 12, 13, 16, 18, and 20 - 35 are cancelled without prejudice. New independent Claim 37 and dependent Claim 38 have also been added. Support for these amendments is found in the Claims as filed. The Examiner is respectfully requested to reconsider and withdraw the rejection(s) in view of the amendments and remarks contained herein.

Restriction Requirement

Applicants affirm the election by telephone on July 8, 2003 to prosecute the invention of Group I, Claims 1 - 23 and 36. Applicants affirm withdrawal, without prejudice, of Group II, Claims 24 - 35 as drawn to a non-elected invention.

Rejection Under 35 U.S.C. §103

Claims 1 - 23 and 36 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Hiroaki Otsuka et al. (JP63-183154) in view of Ullakko, et al. (WO 97/03215). This rejection is respectfully traversed. A copy of the full publication of JP 63-138154 is attached, along with an English-language translation.

Applicants respectfully submit that the amended and new independent claims distinguish over the art of record. In this regard, JP 63-183154 (Otsuka) affirmatively teaches addition

nickel and carbon to shape memory alloys. (See page 7, first full paragraph, of the attached English-language translation of the full reference.) Similarly, WO 97/03215 (Ullakko) also teaches the addition of nickel and carbon to shape memory alloys. In this regard, *Ullakko* states that "Carbon has been selected as an alloying component, because it reinforces and stabilizes austenite and improves the shape memory effect. Contents of less than 0.001% have no effect on the properties." *Id*, at page 8, lines 16 – 18. *Ullako* also states, "Nickel stabilizes austenite strongly and improves the corrosion resistance of steel and its high temperature oxidation resistance. At contents of less than 0.1%, the effects are insignificant." *Id.*, at page 7, lines 21 – 23.

By contrast, the specification of the present invention states at page 6 paragraph 9, "... the alloy does not contain significant amounts of materials that degrade performance. Preferably, in such embodiments, the alloys do not contain significant amounts of C (carbon) or Ni (nickel)." This specification text is antecedent for the limitations on Ni and C to insignificant trace amounts in the claimed alloys. Thus, *Ullakko* and *Otsuka* teach away from Applicants' invention.

Furthermore, neither *Ullako* nor *Otsuka* teach the specific selection of compositional elements of Applicants' invention. As the Examiner notes, the ranges of Mn, and Cr overlap or fall within the ranges of these elements broadly suggested in *Otsuka*. These references do not, however, teach the selection of specific ranges to yield shape memory alloys having essentially 100 percent shape recovery.

Otsuka says nothing at all about the degree of shape memory effect observed with the alloys disclosed. Moreover, *Otsuka* also makes no reference to the use of nitrogen in such alloys.

While *Ullakko* does discuss the use of nitrogen, *Ullakko* discloses very broad ranges of compositions, and generally characterizes the best of those alloys (Class 1) as only having shape recovery rates of only "greater than 70%." *Ullakko*, at page 13, line 24. Moreover, the discussion of shape memory properties in *Ullakko* underscores the unpredictability of the effect of composition on properties. Most of the compositions of *Ullakko* comprise nickel, several contain carbon, and many have levels of chromium higher than those of Applicants' compositions. The shape recovery rate of some of these combinations was in the range of only 30 to 70% (Class 2). *Ullakko*, at pages 13 – 15, and Table 3. Applicants submit that one cannot glean any teaching from this data for the selection and ranges of elements to form alloys having essentially 100% shape recovery with no more than two training cycles.

Conclusion

The cited references either (a) do not suggest the invention of amended Claims 1 and 11 and new Claim 36 or (b) teach away from the these Claims. Applicants respectfully submit that these claims and that, by dependence, Claims 5, 7, 8 – 10, 14, 15, 17, 19, 21, and 37 are patentably distinguished over *Otsuka* in view of *Ullakko*, and that, accordingly, the respective rejections under 35 U.S.C. § 103(a) should be withdrawn. If the Examiner believes that personal communication will expedite prosecution of this application, the Examiner is invited to telephone the undersigned at (248) 641-1600.

Respectfully submitted,

Dated: 20 October 2003

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⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　昭63-183154

⑤Int.Cl.⁴　識別記号　庁内整理番号　⑬公開　昭和63年（1988）7月28日

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38/00　302　V-7147-4K
G 01 K 11/00　M-7269-2F ※審査請求　未請求　発明の数 2　（全4頁）

⑭発明の名称　鉄基の形状記憶合金を用いた温度検出端

㉑特　願　昭62-11362
㉒出　願　昭62（1987）1月22日

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最終頁に続く

明　細　書

1.発明の名称

鉄基の形状記憶合金を用いた温度検出端

2.特許請求の範囲

(1) 重量%としてSi 3.5～8%，Cr 10%以下を含有し、残部はMn，Feおよび不可避不純物よりなるFe－Mn－Si系形状記憶合金に於て、Mn含有量を20～40%の範囲内に変化させMn量に応じて変態温度を50℃から300℃間の所望の温度にコントロールした形状記憶合金を用いることを特徴とした鉄基の形状記憶合金を用いた温度検出端。

(2) 重量%としてSi 3.5～8%，Cr 10%以下に加えてNi 10%以下，Co 10%以下、Mo 2%以下、C 1%以下，Al 1%以下，Cu 1%以下の1種または2種以上を含有し、残部はMn，Feおよび不可避不純物よりなるFe－Mn－Si系形状記憶合金に於て、Mn含有量を20～40%の範囲内に変化させMn量に応じて変態温度を50℃から300℃間の所望の温度にコントロールした形状記憶合金を用いることを特徴とした鉄基の形状記憶合金を用いた温度検出端。

3.発明の詳細な説明

（産業上の利用分野）

この発明は、形状記憶合金を用い食用油、機械油または機械本体等の50～300℃の範囲の温度を簡便に感知する検出端に関するものである。

（従来の技術）

各種の物体の温度、例えば50℃から300℃の範囲の温度を計測する方法は水銀温度計、熱電対、バイメタル等を用いて測温している。

しかし、水銀温度計は簡便に測温することは出来るが、ガラスを用いるため破損防止のための注意が必要のことと最高200℃附近が限界であるため200℃から300℃附近の測温が出来ない。また熱電対やバイメタルの様に電気的信号を温度に転換して測温する方法はそのための専用の設備が必要であり任意の場所を任意の時点で簡便に測温することは出来ない。

次に形状記憶合金を用いた簡便な温度検出方法が特開昭57－212722号公報、特開昭58－40720号

公報、特開昭58－146824号公報において開示されているが、特開昭57－212722号公報による発明の場合は使用温度が示されていないけれども水中で使用する方法であるため、使用温度は１００℃以下と考えてよく、また特開昭58－40720 号公報による発明の場合は動作温度が６７℃の場合についての実施例が示されている。更に特開昭58-146824号公報による発明の場合は使用合金がNi－Ti系であること、逆変態温度が－４０℃～１１０℃であり、この範囲の適当な温度を選定で来るとしている。また各種の公知文献によれば表１に示したように逆変態温度、即ち形状回復温度は１００℃以下或いは５００℃ないし６５０℃であり、１００℃～５００℃の温度範囲について検出することは出来ない。また本発明のようにFe－Mn－Si系の形状記憶合金を用いた例の記載も見当らない。

表　1

形状記憶合金	逆変態温度(℃)[4]	文献
Ni－Ti系（古河ＮＴ合金）	－１０～１００[1]	1) 日経ニューマテリアル 1986 2－24 №6
Cu－Zn－Aℓ（三菱金属ﾒﾓﾘｱﾝ100）	－１００～１００[1]	2) 日経産業新聞 1986 12/5 3) 日本金属学会 1985
Fe－Ni－C（金材研 梶原節夫）	５００（急熱）[2] ６００～６５０[3]	秋期講演大会予稿集 P.92

4) 逆変態温度はマルテンサイト相から母相への変態温度を示し、形状回復温度に相当する。

（発明が解決しようとする問題点）

簡便な温度検出方法として形状記憶合金を使用する方法は伸び回復素子、縮み回復素子または曲げ回復素子を被測温体に接触させて形状回復の状態により温度を感知することができるので、簡便であり、かつ検出端の形状を被測温体に合せて作ることも可能であるため非常に応用範囲の広い方法である。しかしながら１００℃から５００℃の範囲については表１に於て明らかなように測定することが出来ない。

（問題点を解決するための手段）

本発明は従来の形状記憶合金より逆変態温度の高いFe－Mn－Si系の形状記憶合金を用いてMn含有量を変化させ、逆変態温度を５０℃から３００℃間の所望の温度にコントロールした形状記憶合金を温度検出端とすることを特徴とする。

形状記憶合金の逆変態温度が１００℃以上のものを見い出す目的で発明者等は特開昭61－201725号公報で開示したFe－Mn－Si系の形状記憶合金の逆変態温度が高いことに着目し成分含有量と逆変態温度との関係を調査した。その結果、逆変態温度はMn含有量に逆比例することを見い出した。尚Mn含有量が２０％未満或いは４０％を超える場合は形状記憶効果が低下する。その１例として第１図にFe－Mn－Si系形状記憶合金X Mn６Si５Cr（重量％（以下％）としてX ％のMn，６％のSi，５％のCrを含有したFe－Mn－Si系形状記憶合金）の逆変態温度に及ぼすMn含有量の関係を示す。図中点線は逆変態開始温度即ち形状回復開始温度を、実線は逆変態終了温度即ち形状回復終了温度を示す。例えばMn２５％，Si６％，Cr５％，残部Feの場合は第１図の横軸のMn２５％の位置から垂直に線を伸ばし、点線と実線の交点１４５℃で逆変態が開始し、２１０℃で逆変態が終了する。従って温度検出端としては伸び回復素子、縮み回復素子または曲げ回復素子のいづれを用いてもよいが、それぞれの回復素子の特徴を生かして形状回復開始の１４５℃から、形状回復終了の２１０℃までの任意の温度を検出することが可能となる。

逆変態温度はSi，Crの含有量を若干変えること

により逆変態温度を50℃から300℃に広げることが可能であることを見い出した。またNi, Co, Mo, C, AlおよびCuは形状記憶特性、靭性、熱間加工性および耐食性の向上に必要な元素であり逆変態温度を50℃から300℃に変化させることによる上記材質の劣化防止を目的として添加される。尚特許請求の範囲で示したSi, Cr, Ni, Co, Mo, C, AlおよびCuの含有量の制限はいづれも形状記憶合金の記憶特性を向上させるために定めたものである。

温度検出端の形状としては種々の形状が考えられ、特定出来ないが、例えば使用目的に応じ箔、板、線、コイル等に加工された本発明による形状記憶合金を逆変態点以下の温度(例えば常温)で変形した後、被測温体に接触もしくは直近の雰囲気にさらすことで測温を実施する。この時の形状記憶素子としては伸び回復素子、縮み回復素子或いは曲げ回復素子のいづれを用いてもよい。

(実施例)

以下に本発明の実施例を示す。

実施例1

第2図はコイル1にMn25%, Si6%, Cr5%, 残Feの組成から成る本発明による形状記憶合金を用いた天麩羅油の温度検出端である。300〜600℃の温度でコイル1を縮んだ状態で数秒から数十分拘束しておき、その形態を記憶させる形状記憶処理を行った。2はコイル1を引き伸ばすための柄、3は油に浸漬して温度を感知する部分であり、これは金属製の筒4により保護されている。コイル1の先端は金属製筒4に固定され、また金属製筒4のコイル1とは反対側に窓5があり柄2に設置された温度表示物の色が識別出来る構造となっている。この実施例における逆変態温度((逆変態開始温度+逆変態終了温度)/2)は180℃である。

この温度検出端の使用法は次の手順により行う。

① 本発明による形状記憶合金で作られたコイル1を常温において柄2を引くことにより伸び変形させる。

②温度感知部3を天麩羅油に浸す。

③ 油の温度が180℃になるとコイル1が形状回復し温度表示窓に適温になったことを示す色(例えば赤色)があらわれ、温度が適温になったことを感知する。勿論色を目盛にすることも可能である。

尚、この検出端は本発明による形状記憶合金から成るコイル1の組成を変えることにより50〜300℃の液体の温度の検知に使用することが可能である。

実施例2

組成としてMn25%, Si6%, Cr5%, Mo1%, 残りFeである本発明による形状記憶合金の箔(20〜50μ)に実施例1で示した形状記憶処理をほどこし、これを適当な大きさに切り取り、常温にて曲げ変形を行う。本曲げ回復素子の逆変態温度は180℃である。この曲げ回復素子を実施例1の場合と同様に天麩羅油に浸漬する。天麩羅油の温度が180℃に達すると形状が回復し、適温になったことを感知する。

勿論合金組成を変えることにより50〜300℃の液体の温度或いは機械、電気部品等の温度を本実施例の曲げ回復素子を用いて測定することが可能である。

また同じ方法で製造した形状記憶合金の薄板をブザーまたは電球、発光ダイオード等を含む警報回路の電気的接点として使用した。警報器周囲の雰囲気温度が180℃に達すると形状が回復し回路が閉じ、ブザーまたは電球、発光ダイオードを作動させ完全に警報器として機能をはたすことが出来た。

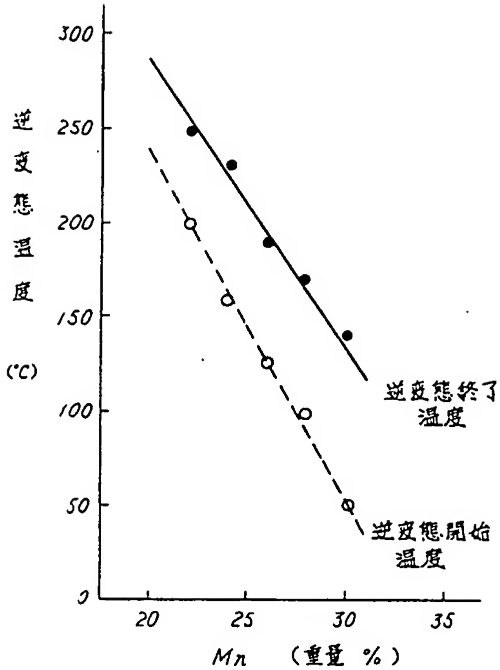
(発明の効果)

本発明により50℃から300℃の温度、特に従来形状記憶合金を用いた測温検出端において検出できなかった100℃から300℃の温度範囲を簡便に検出することが可能となった。

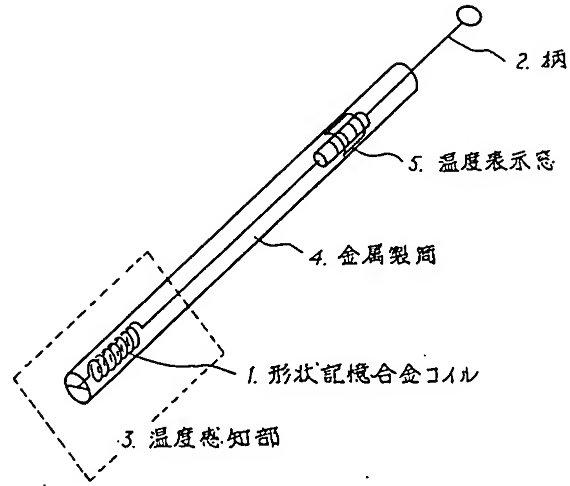
4.図面の簡単な説明

第1図は本発明の形状記憶合金の逆変態温度に及ぼすMn含有量の影響を、第2図は天麩羅油等の液体の温度を検知するための本発明の形状記憶合金を用いた温度検出端の1例を示したものである。

第 1 図



第 2 図



第1頁の続き

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[Translation from Japanese]

(19) Japanese Patent Office (JP)

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(54) Title of the Invention: **Temperature-Detecting Element Using Iron-Based Shape-Memory Alloy**

(21) Patent Application No: 62-11362

(22) Patent Application Date: January 22, 1987

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Specification

1. Title of the Invention

Temperature-Detecting Element Using Iron-Based Shape-Memory Alloy

2. Claims

(1) A temperature-detecting element using an iron-based shape-memory alloy, wherein a Fe-Mn-Si shape-memory alloy is used comprising 3.5 to 8 wt% Si, 10 wt% or less Cr, with the balance being Mn, Fe and the inevitable impurities, and wherein the Mn content is altered within the 20 to 40 wt% range to obtain the desired transform temperature between 50°C and 300°C based on the Mn content.

(2) Temperature-detecting element using an iron-based shape-memory alloy, wherein a Fe-Mn-Si shape-memory alloy is used comprising 3.5 to 8 wt% Si and 10 wt% or less Cr, including one, two or more of the following, being 10 wt% or less Ni, 10 wt% or less Co, 2 wt% or less Mo, 1 wt% or less C, 1 wt% or less Al or 1 wt% or less Cu, with the balance being Mn, Fe and the inevitable impurities, and wherein the Mn content is altered within the 20 to 40 wt% range to obtain the desired transform temperature between 50°C and 300°C based on the Mn content.

3. Detailed Description of the Invention

(Industrial Field of Application)

The present invention relates to a temperature-detecting element using an iron-based shape-memory alloy for easily detecting the temperature of a cooking oil, mechanical oil, or mechanical object within the 50 to 300°C range.

(Prior Art)

The temperature of objects between 50°C and 300°C is usually measured using a mercury, thermoelectric or bimetal thermometer.

A mercury thermometer is easiest to use, but cannot be used at temperatures above 200°C in order to prevent the glass from shattering. As a result, it cannot be used at temperatures between 200°C and 300°C. Thermoelectric and bimetal thermometers convert electric signals to the temperature, but require special equipment. As a result, it is difficult to measure the temperature at the desired place and at the desired time.

Simple temperature-detecting methods using shape-memory alloys have been disclosed in Japanese Unexamined Patent Application Publication [Kokai] No. 57-212722, Kokai No. 58-40720, and Kokai No. 58-146824. The temperature-detecting method in Kokai No. 57-212722 is used in water and, therefore, is used for temperatures up to 100°C. The working example in Kokai No. 58-40720 indicates an operating temperature of 67°C. The invention in Kokai No. 58-146824 uses a Ni-Ti alloy, which has a transform temperature between -40°C and 110°C. As a result, this is the applicable range. The inverse

transform temperatures or shape-recovery temperatures of the shape-memory alloys disclosed in other documents are either less than 100°C or between 500°C and 650°C. As a result, temperatures between 100°C and 500°C cannot be detected. A description of the Fe-Mn-Si shape-memory alloy of the present invention has not been found.

Table 1

Shape-Memory Alloy	Inverse Transform Temp. (%)[4]
Ni-Ti (Furukawa NT Alloy)	-10 ~ 100[1]
Cu-Zn-Al (Mitsubishi Metal Memoriam 100)	-100 ~ 100[1]
Fe-Ni-C (Metallurgist Yoshio Kajiwara)	500 (Rapid Heating)[2] 600 ~ 650[3]

1) Nikkei New Materials 1986 2-24 No. 6

2) Nikkei Sangyo Shimbun 1986 12/5

3) Proceedings of the Japan Metallurgy Society 1985 Fall Meeting P. 92

4) The inverse transform temperature indicates the transform temperature from the martensite phase to the parent phase, and corresponds to the shape-recovery temperature.

(Problem Solved by the Invention)

When a shape-memory alloy is used in a simple temperature-detecting method, an elongated recovery element, compressed recovery element or bent recovery element is brought into contact with the object to be measured, and the shape recovery characteristics are used to determine the temperature of the object. Because the shape of the temperature-detecting element can conform to

the object to be measured, this method has a very wide range of possible applications. However, temperatures in the range between 100°C and 500°C cannot be measured using any of the alloys shown in Table 1.

(Means of Solving the Problem)

The present invention is a temperature-detecting element using an iron-based shape-memory alloy, wherein a Fe-Mn-Si shape-memory alloy is used, and wherein the Mn content is altered within the 20 to 40 wt% range to obtain the desired transform temperature between 50°C and 300°C based on the Mn content.

In order to discover a shape-memory alloy with an inverse transform temperature above 100°C, the present inventors noted the high inverse transform temperature of the Fe-Mn-Si shape-memory alloy disclosed in Kokai No. 61-201725 and studied the relationship between the component amounts and the inverse transform temperature. As a result, they discovered an inverse relationship between the Mn content and the inverse transform temperature. The shape-memory effect decreased when the Mn content was below 20 wt% or above 40 wt%. FIG 1 is a graph showing the relationship between the Mn content and the inverse transform temperature of Fe-Mn-Si shape-memory alloy X Mn 6 Si 5Cr (a Fe-Mn-Si shape-memory alloy containing X wt% Mn, 6 wt% Si and 5 wt% Cr). In the graph, the dotted line indicates the initial inverse transform temperature or initial shape recovery temperature, and the solid line indicates the final inverse transform temperature or final shape recovery temperature. In the case of 25 wt% Mn, 6 wt% Si, 5 wt% Cr with the balance being Fe, a line

extending vertically from the Mn 25% position on the x-axis of FIG 1 intersects the dotted line and the solid line at an initial transform temperature of 145°C and a final inverse transform temperature of 210°C. Therefore, the temperature-detecting element can be an elongated recovery element, compressed recovery element or bent recovery element but, because of the characteristics of the recovery element, it can detect temperature from an initial transform temperature of 145°C to a final inverse transform temperature of 210°C.

The present inventors discovered that the inverse transform temperature could be expanded from 50°C to 300°C by slightly changing the Si and Cr content. Other elements such as Ni, Co, Mo, C, Al and Cu can be added for their shape-memory properties, hardness properties, heat processing properties, and corrosion resistance properties. These elements prevent property deterioration at an inverse transform temperature between 50°C and 300°C. The amounts of Si, Cr, Ni, Co, Mo, C, Al and Cu added in the claims of the present invention are limited to the amounts that improve the memory properties of the shape-memory alloy.

The temperature-detecting element can assume any form, but for the purposes of the present invention the shape-memory alloy should assume box, plate, wire or coil form. After being deformed at a temperature other than the inverse transform temperature (e.g., the ambient temperature), the shape-memory alloy is brought into contact with the object to be measured or brought as close as possible in the surrounding environment. At this time, the shape-

memory element should have be an elongated recovery element, compressed recovery element, or bent recovery element.

(Working Examples)

The following is an explanation of working examples of the present invention.

Working Example 1

FIG 2 is an example of a temperature-detecting element with a Mn 25 wt%, Si 6 wt%, Cr 5 wt%, and Fe balance shape-memory alloy of the present invention used in the coil 1 to detect the temperature of a liquid such as tempura oil. In the shape-memory process, coil 1 is compressed for several seconds or several dozen seconds at a temperature between 300 and 600°C in order to remember the shape. Here, 2 is a handle extending from the coil 1, 3 is the portion dipped in the oil to detect the temperature, and 4 is a protective metal tube. The coil 1 is fixed inside the metal tube 4 so the coil 1 is visible inside the metal tube 4 through the window 5. Color marks indicating the temperature are formed on the handle 2. The inverse transform temperature in this working example is (initial inverse transform temperature + final inverse transform temperature)/2 or 180°C.

The temperature detection method using this element has the following steps.

(1) The coil 1 made of the shape-memory alloy of the present invention is drawn out by the handle 2 to become elongated at the ambient temperature.

(2) The temperature-detecting element 3 is immersed in tempura oil.

(3) When the temperature of the oil reaches 180°C, the coil 1 recovers its shape, and the temperature is indicated by the color marking (red marking) in the temperature-indicating window. In this way, the temperature is detected. Of course, the color markings can be to any scale.

By changing the composition of the shape-memory alloy constituting the coil 1 in the temperature-detecting element of the present invention, it can be used to detect the temperature of a liquid between 50 and 300°C.

Working Examples 2

The shape-memory process in Working Example 1 is performed on a box (20 ~ 50 μ) made of a shape-memory alloy of the present invention consisting of Mn 25 wt%, Si 6 wt%, Cr 5 wt% and Mo 1 wt% with the balance being Fe. It is then cut to the appropriate size and bent at ambient temperature. The inverse transform temperature of this bent recovery element is 180°C. The bent recovery element is then immersed in tempura oil in the same manner as Working Example 1. When the temperature of the tempura oil reaches 180°C, it recovers its shape and the temperature is detected.

By changing the alloy composition, the bent recovery element in this working example can be used to detect the temperature of a liquid, machine or electric component between 50 and 300°C.

A thin plate of the shape-memory alloy manufactured in the same way can be used as the electrical contact point in an alarm circuit containing a buzzer, lamp or light-emitting diode. When the ambient temperature reaches 180°C, the alloy recovers its shape, closing the circuit, and operating the buzzer, lamp or light-emitting diode in the alarm circuit.

(Effect of the Invention)

The present invention is easily able to detect temperatures in the range between 50°C and 300°C, especially temperatures in the range between 100°C and 300°C that cannot be detected by temperature-detecting elements using shape-memory alloys of the prior art.

4. Brief Explanation of the Drawings

FIG 1 is a graph showing the relationship between the inverse transform temperature of the shape-memory alloy and the amount of Mn contained in the alloy. FIG 2 is an example of a temperature-detecting element with the shape-memory alloy of the present invention used to detect the temperature of a liquid such as tempura oil.

FIG 1

[X-Axis] Mn (wt%)

[Y-Axis] Inverse Transform Temperature (°C)

Initial Inverse Transform Temperature

Final Inverse Transform Temperature

FIG 2

1 ... Shape-Memory Alloy Coil

2 ... Handle

3 ... Temperature Detector

4 ... Metal Tube

5 ... Temperature Display Window